Development of Flexible/Stretchable Epoxy Film with High Thermal Stability, Especially Suitable for Versatile Printed Electronics Applications

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ABSTRACT

Authors developed two types of novel plastic films based by epoxy resins, having excellent printability for various conductive or dielectric inks without any surface treatments, excellent optical transparency and very low retardations. Flexible type shows very high durability against repeated folding. Stretchable type shows extremely high elongation and recovery. These films are especially recommendable as substrates to various printed electronics applications e.g. foldable displays or lighting devices, stretchable/wearable sensors, etc.

1 INTRODUCTION

"Epoxy Resin" represents various organic compounds which have at least 2 or more epoxy functional groups in one molecule (*Fig.1*) [1]. Polymers by crosslinking of such epoxy resins (hereinafter referred as "epoxy polymers") generally perform excellent adhesion to the most of organic/inorganic materials, high thermal stability, high voltage resistivity (electric insulation), high resistivity against chemical/water corrosion and very low shrinkage at curing process. Per those beneficial properties, epoxy polymers have been applied to adhesives, binders for paints and coats, matrix resins of FRP (fiber-reinforced plastics) and other versatile applications for a long time. Moreover, today epoxy resins are indispensable materials for semiconductor packaging and circuit layers e.g. EMC (epoxy molding compounds), PCB (printed circuit board) and FCCL (flexible Cupper clad layer) materials.

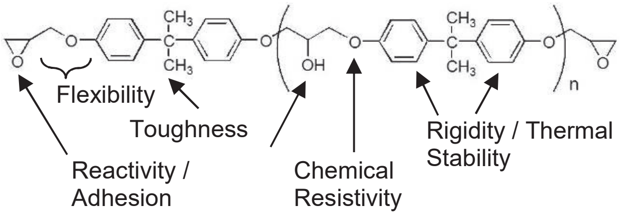


Fig. 1 Generic Structure of Epoxy Resin and its Functional Groups for Various Properties

In this research, authors successfully obtained epoxy films with excellent printability of conductive or dielectric inks even without any treatments for film surface modifications, endowed with various excellent features out of the epoxy polymers as above. These epoxy films also showed excellent optical properties such as high transparency, low yellow index and very low retardation.

Furthermore, noteworthy properties of these epoxy films we have found were very high flexibility enough to survive with repeated folding stress without losing optical properties and keeping excellent adhesion to printed inks on the film. By changing formulation of epoxy resins, we also obtained stretchable films with extremely high elongation and recovery.

2 EXPERIMENT

In general, epoxy polymers are formed by "curing" of epoxy resins by heat treatment or UV irradiation, which perform very high thermal, mechanical and other various properties after curing of resins. Choosing appropriate formulation comprising epoxy resins, cross-linkers, curing accelerators and so on is very important to obtain cured epoxy polymers with required properties upon each usage and applications.

2.1 Preparation of Epoxy Films

High flexible epoxy films were made by varnish of high-Mw type epoxy resins containing some amount of multifunctional epoxy resins and curing accelerators. Stretchable epoxy films were made by varnish of special type epoxy resins with cross linkers commonly used for curing of epoxy resins such as various amines. These epoxy films were prepared by casting of varnish to cure thermally. End of cure for each epoxy film was determined by Tg (glass-transition temperature) change with DSC. Types of experimental epoxy films in this research are shown in *Table 1*.

Table 1 Epoxy Films in This Research

Experimental	A	C	E
Film Type	High Flexible	High Flexible	Stretchable
Epoxy Resin	High-Mw poly BADGE (bisphenol-A diglycidyl ether)	Modified High-Mw type with rigid Segment	Special type with soft segment
WPE (Weight Per Epoxy)	ca. 7,800	ca. 8,000	500~1,000
Film Formation	Varnish to cast	←	←
Treatment	Thermally cured	←	←

3 RESULTS

3.1 Characteristics of High Flexible Epoxy Films

Typical characteristics of epoxy films A and C are shown in *Table 2*.

Table 2 Physical Properties of High Flexible Epoxy Film

Experimental			A	C
Thermal Properties				
Tg		°C	112	170
Td5		°C	357	365
CTE (α1)		ppm	94	71
Mechanical Properties				
Tensile Strength	/ MD	MPa	73	65
	/ TD	MPa	90	71
Elongation	/ MD	%	113	88
	/ TD	%	143	82
Physical Properties				
Water Absorption		%	1.2	0.3
WVTR* (24hr)		g/m^2	30	53
Adhesion (Ag ink)			☺	☺
Optical Properties				
Total Transmittance		%	92	91
Yellow Index			0.5	1.7
In-Plane Retardation		nm	1.8	1.8
Electrical Properties				
Dk (10GHz)			3	2.6
Df (10GHz)			0.031	0.029
Insulation Breakdown		kV	8.8	8.3

* Water Vapor Transmission Rate

3.1.1 Thermal Properties

Tg of the films A and C were observed ca. 110°C and 170°C, respectively. In general, Tg of the cured epoxy polymer comprising rigid molecular structures tends to be higher, and the same tendency was confirmed in this study. Both films A and C showed neither Tm (melting point) nor drastic drop of E' (dynamic elastic modulus) over Tg *(Fig.2)*. 5% weight loss temperature (Td_5) were observed around 360°C by DSC/TGA (10°C/min heating rate). CTE (coefficient of thermal expansion) of these films were observed roughly α1=70~95ppm.

3.1.2 Mechanical Properties

S-S curves of the films A and C are shown in *Fig.3*. Both films A and C showed similar tendency under tension but difference in elongation, which is considered to depend on molecular structure of epoxy resins. Epoxy film C did not break down after 20,000 times of repeated bending (radius r=1mm), and no visible change was observed at the bending point (*Fig. 4*).

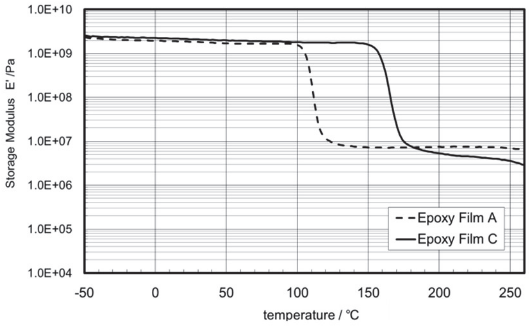


Fig. 2 DMS Curves of High Flexible Epoxy Film

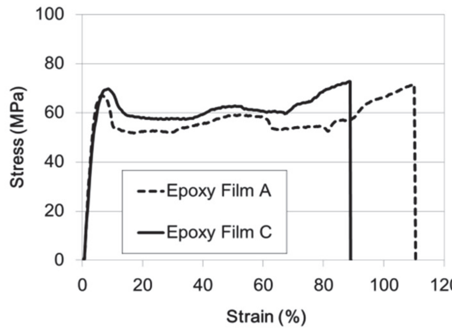


Fig. 3 SS-Curves of High Flexible Epoxy Film

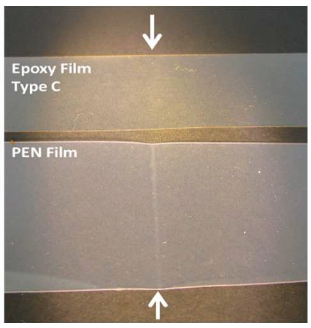


Fig. 4 Epoxy Film after 20k Times of Repeated Bending (r=1 mm)

3.1.3 Optical Properties

Both epoxy films A and C showed very high light transmittance with low yellowness, and excellent optical isotropy. As shown in *Fig. 5*, epoxy film did not show whitening phenomena after annealing, compared to the PET film (which is presumed to be the precipitation of polyester oligomers as crystals) [2].

3.1.4 Other Physical Properties

As shown in Table 2, differences in water absorption and dielectric properties between films A and C were observed, which is considered to depend on the molecular structure of each epoxy resin. Epoxy film C containing very hard hydrophobic unit in the molecule showed very low water absorption and dielectric properties.

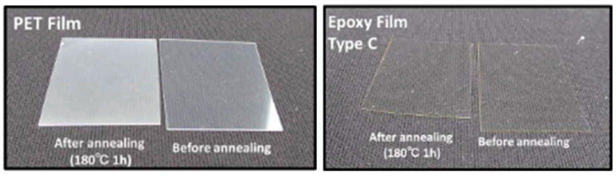


Fig. 5 Comparison of PET Film and Epoxy Film after Thermal Treatment (180°C x 60 min)

3.2 Characteristics of Stretchable Epoxy Films

Typical characteristics of epoxy film E are in *Table 3*.

Table 3 Physical Properties of Stretchable Epoxy Film

Experimental		E
Thermal Properties		
Tg	°C	11
Td5	°C	310
Mechanical Properties		
Tensile Strength / MD	MPa	37.2
/ TD	MPa	36.6
Elongation / MD	%	324
/ TD	%	326
Physical Properties		
WVTR* (24hr)	g/m^2	120
Adhesion (Ag ink)		☺
Optical Properties		
Total Transmittance	%	91
Yellow Index		0.8
In-Plane Retardation	nm	3.3
Electrical Properties		
Insulation Breakdown	kV	12

* Water Vapor Transmission Rate

3.2.1 Thermal Properties

Tg of the film E was observed 11°C, but neither Tm nor drastic drop of E' over Tg could be seen *(Fig.6)*.

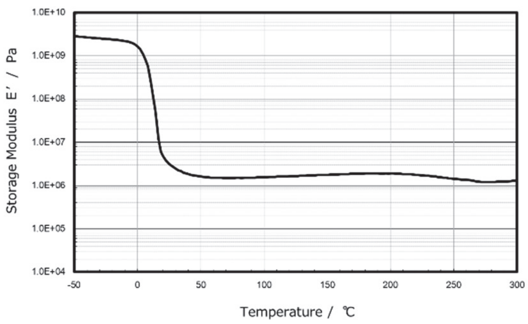


Fig. 6 DMS Curves of Stretchable Epoxy Fílm

3.2.2 Mechanical Properties

S-S curves of the film E is shown in *Fig.7*.

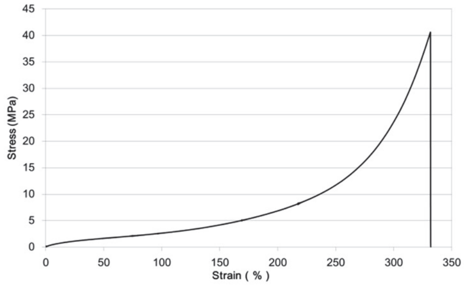


Fig. 7 S-S Curves of Stretchable Epoxy Film

3.2.3 Optical Properties

Epoxy film E showed very high light transmittance with low yellowness. As shown in *Fig. 8*, film E did not show whitening phenomena even under tensile stress.

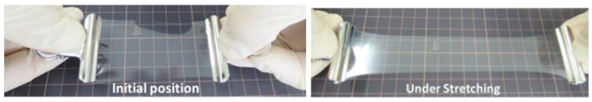
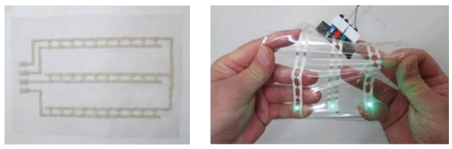


Fig. 8 Stretchable Epoxy Film under Tensile Stress

3.3 Printability of conductive inks onto Epoxy Films

Without any special surface treatment onto these epoxy films (A/C/E), various Ag conductive inks were successfully printed by flexography and then baked at the recommended temperature and time for each ink to obtained circuit patterns. As a result, a very smooth ink layer was formed (*Fig. 9*). Those ink layers showed excellent adhesion to the film and good conductivity. In addition, other conductive inks with nano-metals like Au or Cu, Ag resinate inks, conductive polymer inks like PEDOT: PSS inks, PAS (polyaniline sulfonic acid) inks were tried by not only flexography but also various printing methods like screen printing, adhesion contrast planography, ink-jetting etc., and showed excellent printability and adhesion to epoxy film substrates. As shown in *Fig. 10,* very good formation of OFET layer on epoxy film was reported.



Type C Type E

Fig. 9 Ag Nano-Ink Based Printed Conductive Patterns on Epoxy Films

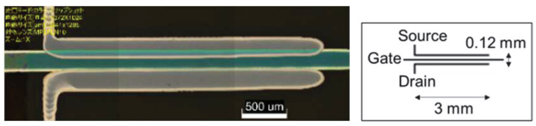


Fig. 10. (Left) Optical Microscope Image of Printed OFET on Epoxy Film (C) and (right) Schematic Drawings of Ag Printed Electrode in the Image (MCC's organic semiconductor is printed at the central part of the image.)

4 DISCUSSION

4.1 Applicability as Printed Electronics Substrates

Dispersed-type inorganic electroluminescence (EL) lighting device was made on epoxy film C, by flexo-printing of Ag nano-ink metal grid and PEDOT: PSS ink as electrode (*Fig. 11*) [3][4][5]. Those EL devices on epoxy film C worked stably and continuously without breakdown even after 20,000 times of repeated bending (r=1mm), substantially no resistivity changes of printed metal grid electrode at the bending point (*Fig. 12*). In addition to its high bending durability of the epoxy film shown in Fig. 4, strong adhesion between the epoxy film and grid electrode layers is considered to keep electrical conductivity even after repeated bending stresses, which may eventually give sufficient foldability of the EL device itself.

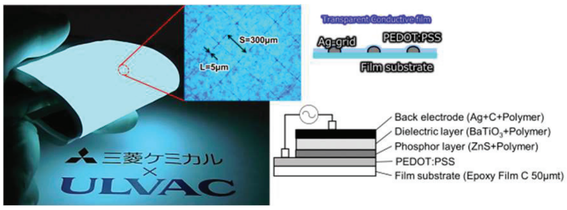


Fig. 11 EL Lighting Device on Epoxy Film (Type C)

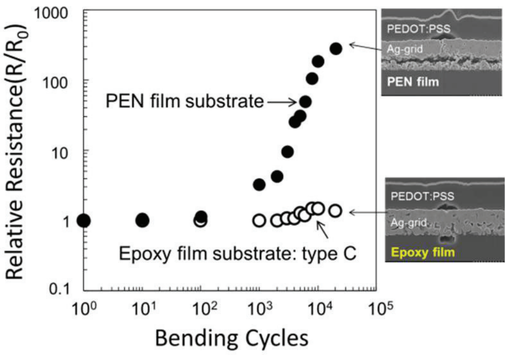


Fig. 12 Comparison of Relative Resistance after Repeated Bending of EL Lighting Device (Epoxy Film Base vs PEN Film Base)

4.2 Applicability of Stretchable Substrates

These epoxy films are not only fitting to additive process like printing of conductive inks but also very well with subtractive process like conventional FCCL per its good chemical resistivity. By using epoxy film E, very flexible and even stretchable circuit can be made easily like *Fig. 9* and *Fig. 13*., subject to flexibility of inks.

4.3 Applicability in Display Film Uses

Other than printed electronics uses, these epoxy films are also proposed to various display film usages by excellent optical and thermal properties. Furthermore, flexibility of high-Mw epoxy films (A/C) enough to endure after repeated bending stress will be beneficial to new requirements on recent "foldable" display uses.

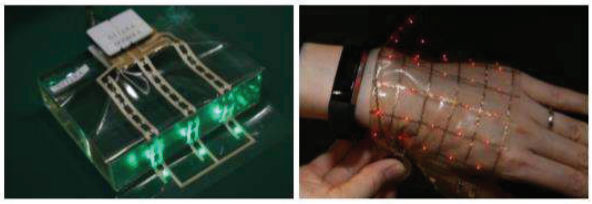


Fig. 13 Additive (Printing) and Subtractive (Cu-etching) Circuit on Stretchable Epoxy Film (E)

5 CONCLUSIONS

In this research, authors successfully obtained various epoxy films with high thermal durability, flexibility or stretchability. These epoxy films also have excellent printability (ink adhesion) for printing processes using various conductive inks, on top of very good mechanical and optical properties unique to typical epoxy resins as thermosetting polymers.

These epoxy films are recommendable for substrates of flexible/stretchable printed hybrid electronics (FHE), such as devices like complicated 3D wirings, flexible displays, wearable sensors or medical electronics, etc.

6 ACKNOWLEDGMENT

Novel printing equipment and technologies to print various conductive metal inks onto these epoxy films for evaluation and demonstration purposes (*Fig. 9,11,13*) were provided by Nihon Denshi Seiki Co., Ltd.

Printed OFET device (*Fig. 10*) was fabricated through collaboration with Prof. Tokito of Yamagata University.

EL lighting devices (*Fig. 11*) consisted with Ag nano inks (*Fig. 12*) were provided by ULVAC Corporation.

REFERENCES

[1] "*Review of Epoxy Resin .1*", (2003), The Japan Society of Epoxy Resin Technology, or any other general

[2] E. Takiyama, "*Handbook of Polyester Resin*", (1988)

[3] M. Ohsawa, N, Hashimoto," Flexible transparent electrode of gravure offset printed invisible silver-grid laminated with conductive polymer", *Mater. Res.* Express 5 (2018) 085030

[4] M. Ohsawa, N, Hashimoto," Flexible and Transparent Silver-Grid Over-Coated with PEDOT: PSS Electrode Prepared by Gravure Offset Printing", ICEP 2018

[5] The Japanese Society of printing Science and Technology, "*Journal of printing science and technology* "(2009) ,46(1),23